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The Role of Aging in Resolving the Ferrocyanide Safety Issue

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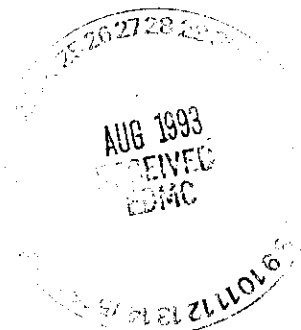
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The Role of Aging in Resolving the Ferrocyanide Safety Issue

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THE ROLE OF AGING IN RESOLVING
THE FERROCYANIDE SAFETY ISSUE

H. Babad
J. E. Meacham
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ABSTRACT

A chemical process called aging, in which stored ferrocyanide waste could be dissolved and dispersed among waste tanks, or destroyed by radiolysis and hydrolysis, has been proposed at the Hanford Site. This paper summarizes the results of applied research, characterization, and modeling activities on Hanford Site ferrocyanide waste material that support the existence of a chemical aging mechanism. Test results from waste simulants and actual waste tank materials are presented and compared with theoretical estimates. Chemical and energetic behavior of the materials are the key indicators of destruction or dispersion. Screening experiments on vendor-prepared sodium nickel ferrocyanide and the initial results from core sampling support the concept that aging of ferrocyanide is taking place in the waste tanks at the Hanford Site. This report defines the concept of waste aging and explains the role that aging could play in resolving the Hanford Site ferrocyanide safety issue.

LIST OF TERMS

AA	Atomic Absorption
DSC	Differential Scanning Calorimetry
DST	Double-Shell Tank
EDS	Energy Dispersive Spectroscopy
ESEM	Environmental Scanning Electron Microscopy
FY	Fiscal Year
IC	Ion Chromatography
IR	Infrared
PNL	Pacific Northwest Laboratory
SST	Single-Shell Tank
TBP	Tributyl Phosphate
XRD	X-Ray Diffraction

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1.0 INTRODUCTION

Public Law 101-510, Section 3137, requires development of plans to resolve safety issues associated with high-level waste tanks at the Hanford Site (PL101-510 1990). Of particular concern are events that could lead to excessive temperature changes or pressure increases resulting in a release of radioactive material. Fifty-four tanks have been identified and categorized by tank contents as potential safety concerns. These include tanks that (1) contain ferrocyanide compounds; (2) have the potential for flammable gas generation; (3) contain organics; or (4) have high-heat loads. The ferrocyanide and hydrogen gas safety issues have been declared unreviewed safety questions (DOE 1991) because postulated accident scenarios may fall outside safety envelopes as defined by existing safety analysis documentation.

Since the 1940s, radioactive waste from defense operations has been accumulating in underground high-level waste tanks at the Hanford Site. There are 177 of these waste tanks: 149 single-shell tanks (SSTs), and 28 double-shell tanks (DSTs). With the increased emphasis on defense materials production in the early 1950s, it became necessary to increase the available waste tank storage volume while minimizing construction of new tanks. A process was developed that allowed disposal of large volumes of low-activity liquids to cribs and trenches. The treatment involved scavenging ^{137}Cs and ^{90}Sr from uranium recovery plant waste using ferrocyanide and other chemicals in a carrier precipitation process. This action reduced the waste volume in the tanks by over 40 million gallons, and minimized the amount of long-lived radionuclides discharged to the ground.

Ferrocyanide is a complex of ferrous ion and cyanide that is considered nontoxic because it is stable in aqueous solutions. However, in the presence of oxidizing materials, such as nitrates/nitrites, near-stoichiometric amounts of ferrocyanide can be made to explode under special conditions in the laboratory by (1) heating it to high temperatures (above 285 °C); or (2) by an electrical spark of sufficient energy to heat the mixture. The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo an uncontrolled exothermic reaction had not been thoroughly studied until recently. Because the scavenging process involved precipitating ferrocyanide from solutions containing nitrate and nitrite, it is likely that an intimate mixture of ferrocyanides with nitrates and nitrites exists in parts of some of the Hanford Site SSTs.

Known or suspected major constituents of the ferrocyanide waste include: sodium nitrate; sodium nitrite; metal silicates; alkali metal hydroxides; phosphates; sulfates; carbonates of iron; calcium and other metals; ferrocyanide and uranium salts; and fission products created by processing irradiated fuel. Alkaline aluminum cladding waste was later added to some of

the ferrocyanide tanks and may have become mixed with the ferrocyanide sludge. Based upon flowsheet data and process records, there are different types of ferrocyanide tank waste.

Three flowsheets were used to scavenge the radionuclides from aqueous waste. The T Plant flowsheet was used to treat first-cycle waste from the bismuth-phosphate process. This generated about 10 percent of the total ferrocyanide waste. The U Plant flowsheet treated acid solvent extraction waste after the uranium had been recovered from bismuth phosphate "metal waste" using the tributyl phosphate (TBP) process. The U Plant process produced about 70 percent of the total ferrocyanide waste. The In Farm flowsheet treated the basic "metal waste" previously treated by the TBP process but not scavenged for soluble radionuclide removal. This process produced the highest concentration of ferrocyanide sludge, and accounts for the remaining 20 percent of the total ferrocyanide waste.

The In Farm ferrocyanide waste originated by treating the supernatants of waste that had previously undergone uranium recovery (the TBP process). The waste had been neutralized and sent back to the tanks for settling before cesium and strontium scavenging. Consequently, the In Farm waste contained less inert solids in the waste stream and was more concentrated in ferrocyanide salts than waste treated using the T Plant and U Plant flowsheets.

This report focuses on processes that appear to occur during extended storage of ferrocyanide waste in Hanford Site tanks. It defines the concept of waste aging and focuses on the role that such processes could play in closing the ferrocyanide safety issue. The report summarizes the results of applied research, characterization, and modeling activities on ferrocyanide waste material. It also provides the results of theoretical estimates and studies on waste simulants and actual tank material that focus on the task of destroying some of the ferrocyanide inventory in Hanford Site waste tanks.

2.0 CONCEPT OF WASTE AGING

The aging of ferrocyanide waste is broadly defined in terms of those processes that result in a lower potential for ferrocyanide reactions. This includes dissolution and removal of ferrocyanide during liquid transfers, or degradation of the ferrocyanide to a less energetic form by hydrolysis and/or radiolysis. A detailed review of literature relating to ferrocyanide aging is scheduled to be released at the end of fiscal year (FY) 1993.

Insoluble sodium nickel ferrocyanide, the major component of the ferrocyanide sludges formed during the radioisotope scavenging campaign, will dissolve in a caustic solution containing 0.01 $\underline{M}$ hydroxide. This has been demonstrated using relatively pure vendor-prepared material in alkaline salt solutions (Lilga et al. 1992). The rate of dissolution increases with increasing hydroxide concentration (see Section 3.2). Dissolution of sodium nickel ferrocyanide results in soluble sodium ferrocyanide and a nickel hydroxide precipitate via equation 1.

$$Na_2NiFe(CN)_6(s) + 2\,NaOH \rightarrow Na_4Fe(CN)_6 + Ni(OH)_2\downarrow$$

$$(1)$$
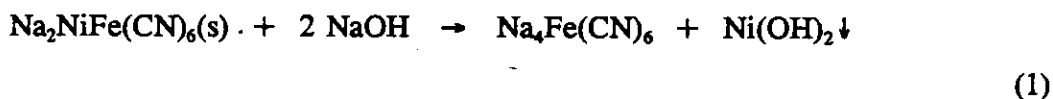
Soluble ferrocyanide is a byproduct of many industries, including aluminum manufacturing, iron and steel making, metal finishing (Robuck and Luthy 1979), and chemical manufacturing. Because ferrocyanide wastes are not uncommon, several papers have been written on alkaline hydrolysis reactions involving ferrocyanide. Research (Robuck and Luthy 1979) using spent potlining leachate has demonstrated that ferrocyanide will hydrolyze to form formate, ferric oxide, and ammonia (see equation 2). Similar reactions should be possible in the alkaline conditions found in the ferrocyanide SSTs. The reaction was found to be first order with respect to cyanide, and zero-order with respect to hydroxide for pH values greater than 10 (Robuck and Luthy 1979).

$$6\,Fe(CN)_6^{4-} + 12\,OH^- + 66\,H_2O + O_2 \rightarrow 36\,HCOO^- + 2\,Fe_3O_4\downarrow + 36\,NH_3\uparrow$$

$$(2)$$
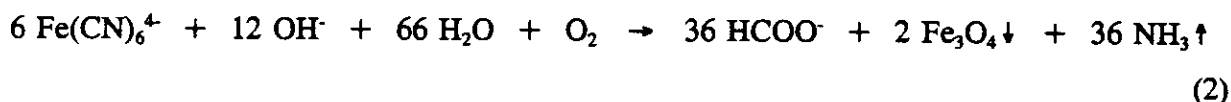
The literature (Wiegand and Tremelling 1972) suggests that hydrolysis is actually a two-step process. The ferrocyanide dissociates to free cyanide, which is then hydrolyzed to form formate and ammonia (see equations 3 and 4 [Wiegand and Tremelling 1972]). The hydrolysis reaction is very temperature dependent. The reaction proceeds slowly at room temperature, with a three-fold increase in reaction rate for every 10 °C rise in temperature.

$$Fe(CN)_6^{4-} + H_2O \rightarrow Fe(CN)_5H_2O^{3-} + CN^-$$

$$(3)$$

$$CN^- + 2\,H_2O \rightarrow HCOO^- + NH_3\uparrow$$

$$(4)$$
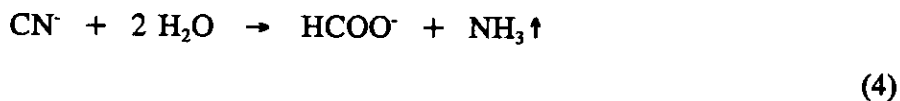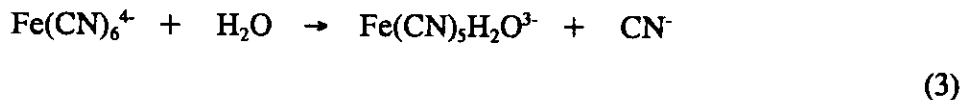
The effect of γ-radiation on ferrocyanide solutions has been investigated, but offers very complex chemistry. The decomposition of water by ionizing radiation yields radical and molecular products (see equation 5). In turn, these products can react to reduce or oxidize ferric or ferrous iron in solution. It has been demonstrated that, whereas ferrocyanide is oxidized in aerated acid solution, ferricyanide is reduced at pH greater than 11 (Hughes and Willis 1961). However, no mechanism was put forward to account for these observations.

$$H_2O \longrightarrow H\cdot, \cdot OH, H_2, H_2O2 \text{ (etc.)}$$

(5)
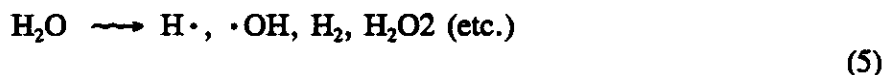
Recent experiments at Pacific Northwest Laboratory (PNL) suggest that soluble ferrocyanide salts produce cyanide ions by radiolysis (Lilga et al. 1992). This may lead to an increase in the rate of hydrolysis; however, it is unknown whether radiolysis plays an important factor in aging of Hanford Site ferrocyanide waste. Little is known about the effect of γ-radiation on insoluble complex ferrocyanide salts, although degradation by ultraviolet radiation has been observed in ferrocyanide compounds (Ohno and Tsuchihasi 1965; MacDiarmid and Hall 1953; Masri and Haissinsky 1963).

To validate the aging concept, two events must be evident. First, the postulated mechanisms must be demonstrated on flowsheet waste simulants and eventually on real ferrocyanide waste. Second, a means of delivering the alkali to the ferrocyanide-precipitated waste must be shown. Experimental data must confirm that initially insoluble ferrocyanide salts will dissolve and/or degrade under conditions known to have existed in the ferrocyanide tanks.

The slow diffusion of materials in aqueous heterogeneous waste systems is known to occur; however, the time required for such diffusion is long. Questions remain whether a diffusion-controlled process could dissolve waste near the bottom of the tank. Modeling and perhaps some experimental studies are needed to determine the time required for diffusion of alkali through the deepest bed of settled waste.

Mechanisms for accelerated mixing in the tanks have been postulated. Three tank circumstances are worth noting: (1) some solutions added to the ferrocyanide tanks were of higher specific gravity than the solutions produced during cesium precipitation -- resulting in a higher density liquid covering a lower density liquid; (2) vertical temperature profiles have revealed temperature gradients between the waste surface and the tank bottom; and (3) radiolysis of water results in the formation of hydrogen gas. Differences in liquid densities, temperature gradients, and the upward migration of gas bubbles through the sludge could all contribute to microconvective mixing in the ferrocyanide waste tanks. The possibility that such a microconvection phenomenon might exist is supported by discussions with Professors Pigford and Chamber at the University of California, Berkeley, who are international authorities on diffusion and mixing phenomena in porous media.

3.0 INVESTIGATION OF AGING

3.1 FERROCYANIDE TANK HISTORY

Although the precipitation of sodium nickel ferrocyanide was done at slightly alkaline conditions (pH = 8.5 - 10), historical data indicate that the ferrocyanide tanks were used for a variety of waste management operations that exposed the tanks to alkaline waste. Highly alkaline reprocessing waste from the caustic dissolution of aluminum cladding and/or highly alkaline evaporator bottoms from waste concentration operations were added to many of the ferrocyanide tanks (Anderson 1990).

In 1992, an analysis of the SSTs was made to assess possible impacts of low pH on a variety of potential tank reactivity hazards. An excerpt from the alkalinity data obtained during this effort is presented in Table 3-1 (for complete details, refer to Table B-2 in WHC-EP-0347, Supplement [Ryan et al. 1992]). Historic data for the ferrocyanide tanks suggest that most of the tanks are alkaline, with a hydroxide concentration greater than 0.1 $\underline{M}$.

Values for pH presented in Table 3-1 contain considerable error. Ionic strength in the supernatant and drainable liquid samples exceeded 4.0 $\underline{N}$, making a direct correlation between hydrogen ion activity and concentration meaningless. Therefore, the pH data are presented as a relative measure of acidity among the high ionic liquid samples. The hydroxide concentration measurements presented are a more reliable measure of alkalinity. Hydroxide concentrations were measured by direct potentiometric titration of the solutions with a standardized acid.

Depending on the waste tank, large volumes of various waste types were transferred in and out of the tank during its active life. To prevent leaks, there has been an ongoing stabilization program of saltwell pumping in the SSTs to transfer drainable liquid to the DSTs. This may have dispersed ferrocyanide among several tanks. A total of 106 SSTs have been stabilized, including 17 of the 24 ferrocyanide tanks.

Another important parameter in the aging process is temperature. Higher temperatures lead to faster dissolution and hydrolysis. The current bulk temperature of the ferrocyanide tanks ranges between approximately 20 to 55 °C. Temperatures in the tanks have dropped steadily since the scavenging campaign ended, and the highest current temperature is in tank 241-BY-104 (approximately 55 °C). However, temperatures have historically been much higher. Temperature data from 1961 to 1964 show C Farm ferrocyanide tanks with temperatures ranging between 66 and 82 °C (Mercier et al. 1981). Temperatures in BY Farm tanks have been even higher, ranging between 66 and 93 °C from 1974 to 1980 (Grigsby et al. 1991).

Table 3-1. Ferrocyanide Tank Waste Alkalinity*.

	pH	OH, $\underline{M}$	Sample Date	Notes
BY-105	13.3	0.78	11/90	Supernatant
BY-111	9.6	NA[1]	6/56[2]	
C-108	11.8	0.48	9/75	Supernatant
C-109	13.7	0.5	11/90	Supernatant
C-112	12.1	0.67	11/74	
	11.9	0.49	6/75	
	9.0 - 10.5	NA	3/92	Water leach of core segments[3]
T-101	13.0	0.27	3/75	Supernatant
	13.3	0.21	9/89	
T-107	13.2	0.16	3/65	Supernatant
	12.3	0.08	9/75	
	11.1	0.025	9/89	
TY-101	12.7	0.05	12/82	
	10.0	NA	9/85	Water leach of core composite
TY-103	12.0	0.24	3/65	Supernatant
	11.7	NA	2/72	
	9.5 - 12.2	0 - 0.017	9/85	Drainable liquid
TY-104	12.0	0.32	3/65	
	12.1	NA	2/72	
	12.1 - 12.2	0.013 - 0.016	8/85	Drainable liquid

[1]NA = Not available.
[2]A more recent sample has not been found.
[3]Water leach of 1 g of core sample with 100 g of water.

*Ryan et al. 1992

3.2 FERROCYANIDE WASTE SIMULANTS

Simulated ferrocyanide sludge, representative of that formed during the scavenging campaign, was prepared using original flowsheets (U Plant, In Farm, and T Plant). No radioactive isotopes were used in the simulant preparation; however, nonradioactive cesium was added to the In Farm simulant. The U Plant flowsheets represent 70 percent of the ferrocyanide that was used at the Hanford Site and found in 17 of the 24 Ferrocyanide Watch List tanks. The In Farm flowsheet waste was placed into 4 tanks and accounts for 20 percent of the total ferrocyanide added.

The third scavenging campaign employed used was the T Plant flowsheet, which accounts for 10 percent of the ferrocyanide that was added to the waste tanks. This waste was put into 4 tanks, including one tank (241-TK-118) that also received U Plant flowsheet waste. Tests using this simulant are scheduled during the last half of FY 1993.

Tests were conducted on U Plant and In Farm simulant dried under vacuum at 60 °C for 24 hours. U Plant simulant did not exhibit explosive reactions even when heated to 500 °C. Adiabatic calorimetry tests revealed that dry U Plant simulant will self heat from 270 to 620 °C. The In Farm simulant exhibited slow propagating reactions (5 to 10 cm/min) when externally heated to 245 °C. This is equivalent to a burn, and is much slower than a detonation (>300 m/s). A summary of the heat of reaction recorded during adiabatic calorimetry tests is presented in Table 3-2.

Table 3-2. Heats of Reaction of Various Simulants*.

Material	Heat of reaction[1]
$Na_2NiFe(CN)_6$	-945 cal/g of dry material
U Plant 2 Simulant	-84 cal/g of dry material
In Farm 1 Simulant	-250 cal/g of dry material

[1]Values on a dry basis with all free water removed. Samples still contained approximately 2 to 3 wt% chemically bound water.

*Fauske 1992

The highest fuel (as sodium nickel ferrocyanide) content in the simulants was determined to be less than 26 wt% on a dry basis. Propagation experiments on the simulants showed that greater than 13 wt% fuel and less than 12 wt% moisture was required to sustain a propagating reaction (Fauske 1992).

The concentration limit for ferrocyanide propagating reactions in actual waste must still be established by laboratory investigations. Tank waste analyses can then be used to demonstrate that this concentration is not exceeded within the waste. Sampling and subsequent analysis, combined with modeling, should provide the technical basis for removing tanks from the Ferrocyanide Watch List. If this is not possible, then moisture and/or temperature control may be required to ensure in situ safe storage.

3.3 FERROCYANIDE TANKS 241-C-109 AND 241-C-112 CHARACTERIZATION RESULTS

Core samples obtained from ferrocyanide tanks 241-C-109 and 241-C-112 have been analyzed. These tanks received wastes from the In Farm flowsheet and should contain the highest concentration of ferrocyanide. Analyses were performed on quarter segments (12.1 cm [4.75 in.] slices) so that the effect of layering could be evaluated. A brief comparison between characteristics of quarter segment samples extruded from tank 241-C-112 and simulant material is presented in Table 3-3. With the noted exception of total cyanide and energetics, there was good agreement between simulant sludge properties and those observed for actual waste material (Cash et al. 1993; Jeppson and Wong 1993; Simpson et al. 1993).

Preliminary analytical results from core samples of tank 241-C-109 have also shown low energetics. Only one core segment exhibited any exothermic activity, and the rest of the samples contained a moderate to large endotherm in the temperature range where a ferrocyanide exothermic peak was expected. Tank 241-C-109 material appears to be no more reactive than tank 241-C-112 waste.

Low total cyanide and energetic values are significant. Core sampling offers the best evidence to date that degradation has occurred in the ferrocyanide tanks. Total cyanide and energetic values are approximately an order of magnitude lower than predicted by ferrocyanide sludge simulants and flowsheet mass balances. Aging offers an explanation for these findings.

In addition to low energetics and cyanide values, there is more evidence of cyanide hydrolysis. Ammonia is a byproduct of cyanide hydrolysis (see equations 2 and 4). Gas analyses of tank dome spaces have discovered detectable concentrations (> 5 ppm) of ammonia in six of the eight ferrocyanide tanks tested. Ammonia concentrations have ranged from 20 to 255 ppm.

Table 3-3. Comparison of Waste Material from Tanks 241-C-112
and 241-C-109 with Simulants.

Analyte	In Farm Simulant	C-112 Core 34 ¼ Segment	C-112 Core 36 ¼ Segment	C-109 Core 47 ¼ Segment	C-109 Core 48 ¼ Segment	C-109 Core 49 ¼ Segment
Total Cyanide (wt%)[1]	15.7	0.43 to 0.97	0.40 to 0.92	0.30 to 0.55	0.87 to 1.1	0.35 to 0.81
ΔH (cal/g)[1]	-250	-28 to -38	-5 to -11	No Exotherm	-6.2 to -6.7	No Exotherm
Water (wt%)	41 to 50	45 to 58	41 to 64	18 to 39	21 to 40	21 to 40
Density (g/ml)[1]	1.5	1.5 to 1.6	1.3 to 1.6	NA[2]	NA	NA

[1]Values on a dry basis with all free water removed. Samples still contained approximately 2 to 3 wt% chemically bound water.
[2]NA = Not Available.

3.4 PACIFIC NORTHWEST LABORATORY AGING TESTS

Current studies seek to identify aging mechanisms that are taking place in the Hanford Site tanks as a result of exposure to highly alkaline aluminum decladding waste (from the reprocessing of aluminum-clad fuels in the plutonium-uranium extraction process) and highly alkaline evaporator bottoms from concentration of reprocessing waste. Aging processes may have dissolved, diluted, and slowly destroyed the ferrocyanide over the last 35 years. PNL studies are investigating the effects of pH, sodium-ion concentration, gamma radiation, and various anions on solubilization of vendor-prepared sodium nickel ferrocyanide (Lilga et al. 1992; Lilga and Schiefelbein 1993).

In the initial dissolution screening experiments, 1 g of vendor-prepared sodium nickel ferrocyanide was stirred and refluxed for 96 hours in 0.1 $\underline{M}$ and 1.0 $\underline{M}$ NaOH. These experiments were performed in standard laboratory glassware. Table 3-4 summarizes the conditions and results of the two experiments. The data indicate that vendor-prepared material dissolves in high-pH solutions to give insoluble nickel hydroxide and soluble ferrocyanide.

Table 3-4. Conditions and Results for Preliminary Experiments*

Caustic concentration	0.1 $\underline{M}$ NaOH	1.0 $\underline{M}$ NaOH
Initial pH	12.9	13.8
Final pH	10.5	13.0
$Na_2NiFe(CN)_6 \cdot Na_2SO_4 \cdot 4.5\ H_2O$ (g)	1.0005	1.0041
Moles $Fe(CN)_6^{-4}$ or Ni^{+2}	1.85×10^{-3}	1.86×10^{-3}
Weight of recovered solids (g)	0.3316	0.5113
Solution [Fe] (mg/L)	2030	1600
Moles Fe in solution	1.82×10^{-3}	1.43×10^{-3}
Fraction total Fe in solution	98%	77%
Solution [Ni] (Mg/L)	39	3.3
Moles Ni in solution	3.32×10^{-5}	2.81×10^{-6}
Fraction total Ni in solution	1.8%	0.15%
$[NH_3]$ in gas (ppm)	30	375
Approximate moles NH_3 produced	8.04×10^{-8}	2.34×10^{-6}
Approximate %-yield NH_3	0.007	0.02

Atomic absorption (AA) analysis of the reaction supernatants revealed that essentially all of the iron was solubilized after 96 hours at reflux conditions. Very little of the nickel was found in the supernatant solutions. Environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) of the soluble solids crystallized from the supernatant are consistent with the AA results, showing the presence of iron but not nickel. Infrared (IR) spectroscopy and x-ray diffraction (XRD) indicated that ferrocyanide ($Fe(CN)_6^{4-}$) is the primary cyanide compound in solution.

Analysis using IR spectroscopy, ESEM, EDS, XRD, and Maussbauer spectroscopy were made to characterize the insoluble solids. ESEM analysis revealed the presence of nickel in the reaction precipitate. Iron was also detected at very low levels. Analysis by IR spectroscopy and XRD showed that the nickel-containing insoluble species is nickel hydroxide. In addition, IR spectroscopy and EDS showed the presence of significant quantities of silica, from etching the glassware used in these experiments. The larger weight of the insoluble solids obtained using 1.0 $\underline{M}$ NaOH is because of a larger amount of silica

*Lilga et al. 1992

etched from the glassware in this sample. For this reason, Teflon* labware was used in subsequent experiments. The Maussbauer spectrum of the insoluble solids from the 1.0 M NaOH dissolution is weak, indicating a low iron content.

In both experiments the presence of ammonia was detected. This indicates indicative of cyanide hydrolysis reactions. A greater degree of hydrolysis occurred in the more basic solution. The extent of hydrolysis was very low. After 96 hours the largest yield of ammonia was 0.02 percent (0.02 percent of the CN groups were converted to NH_3).

A more detailed study was conducted to determine the influence of pH, ionic strength, and the presence of tank waste simulant salts on the rate and extent of dissolution of the vendor-prepared sodium nickel ferrocyanide material. The primary difference between these experiments and the preliminary screening experiments is that they were performed at room temperature in Teflon labware.

A parametric experiment to study the effect of initial pH on ferrocyanide dissolution was conducted at starting pH values of 12, 13, and 14 (0.01 M, 0.1 M, and 1.0 M NaOH, respectively). Solutions were periodically sampled during the reaction and were analyzed for iron by AA (see Figure 3-1). At the end of the experiment, the final pH was measured and the soluble and insoluble solids were analyzed by IR spectroscopy, ESEM, EDS, XRD, and occasionally by Maussbauer spectroscopy. In some cases, the supernatant was analyzed for free cyanide, ferrocyanide, and ferricyanide by ion chromatography (IC).

Figure 3-1 shows that dissolution is 95 percent complete after 0.5 hour of stirring in 1 M NaOH (pH 14) at room temperature. The reaction at pH 12 is base-limited, but the base is rapidly consumed within 0.1 hour. At pH 13, a slight excess amount of base is present and the dissolution proceeds rapidly, at first, but then slows to reach about 85 percent completion in 144 hours. The dissolution would probably continue to completion at longer reaction times at pH 13.

Experiments were performed to determine the effect of solution ionic strength on the dissolution of ferrocyanide. For experiments conducted at the same initial pH, the rate and extent of dissolution tends to be lower at a higher sodium concentration. This was probably caused by a common ion effect in the high sodium-ion medium.

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*Teflon is a trademark of the E. I. duPont de Nemours Company.

Figure 3-1. Solubility of Vendor-Prepared Na₂NiFe(CN)₆ in
NaOH as a Function of pH at 25 °C.
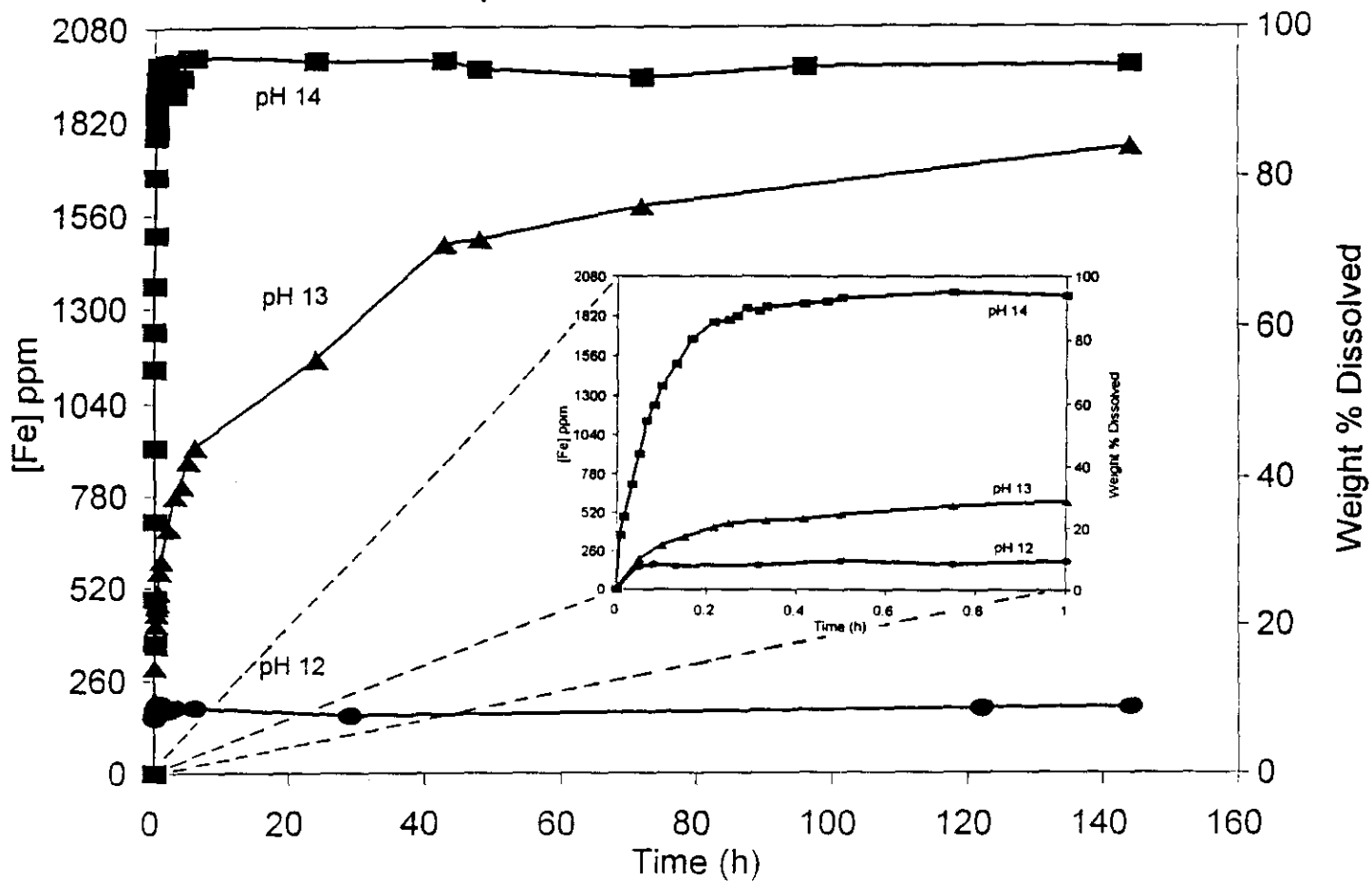
The influence of anions present in the ferrocyanide SSTs was also investigated (see Figure 3-2). Vendor-prepared sodium nickel ferrocyanide was dissolved in a saline solution of tank simulant salts to yield a solution with 1.0 $\underline{M}$ sodium concentration and a pH of 12.8, which was adjusted to pH 13. The results from these experiments showed that ferrocyanide dissolved faster in the pH 13 simulant salt solution than other pH 13 solutions tested. Adding sodium sulfate suppressed dissolution, while adding tank salts enhanced dissolution. The enhanced rate of dissolution with SST simulant salts is thought to be from buffering of the solution by phosphate.

Because the SST contents are not being mechanically mixed, an experiment investigating the dissolution of the vendor-prepared sodium nickel ferrocyanide in the presence of SST simulant salts was conducted under static conditions. The experiment was conducted in Teflon labware at pH 13 with simulant salts added to give 1 $\underline{M}$ sodium ion concentration. To minimize disturbance, the solution was sampled less frequently (24-hour intervals) than the stirred solutions. Prior to each sampling, a 5-second stirring was required to ensure a homogeneous solution phase. As expected, the rate of dissolution is slower in the static solution. Nevertheless, appreciable dissolution occurred. Approximately 40 percent was dissolved after 24 hours with no stirring, and 90 percent was dissolved after 6 days. IC analysis for free cyanide ion showed 9.1 ppm after 72 hours and 11.8 ppm after 144 hours.

Dissolution experiments have shown that the ferrocyanide-cesium compounds are quite insoluble in caustic solutions. Dicesium nickel ferrocyanide and In Farm ferrocyanide simulant were leached for 144 hours at room temperature in solutions containing 0.1 $\underline{M}$ to 4.0 $\underline{M}$ NaOH. AA analysis of the supernatants revealed no soluble cesium. Analyses of the remaining solids confirmed that all of the cesium was still present. Sodium nickel ferrocyanide was solubilized from the In Farm simulant material, but not cesium.

Gamma radiation experiments suggest that gamma radiation does not greatly affect the dissolution reaction. There was no increase in dissolution rate in the gamma pit experiments and similar rates were observed for unstirred irradiated and control solutions. A more complex mixture of iron cyanides in the insoluble fraction was found for the gamma radiated samples. This suggests that an iron cyanide species re-precipitates from solution. Further work is needed to determine if this is indeed the case and to identity the species of the iron cyanide re-precipitate.

Figure 3-2. Solubility of Vendor Material Sodium Ion (Na^+) Dependence, pH 13.
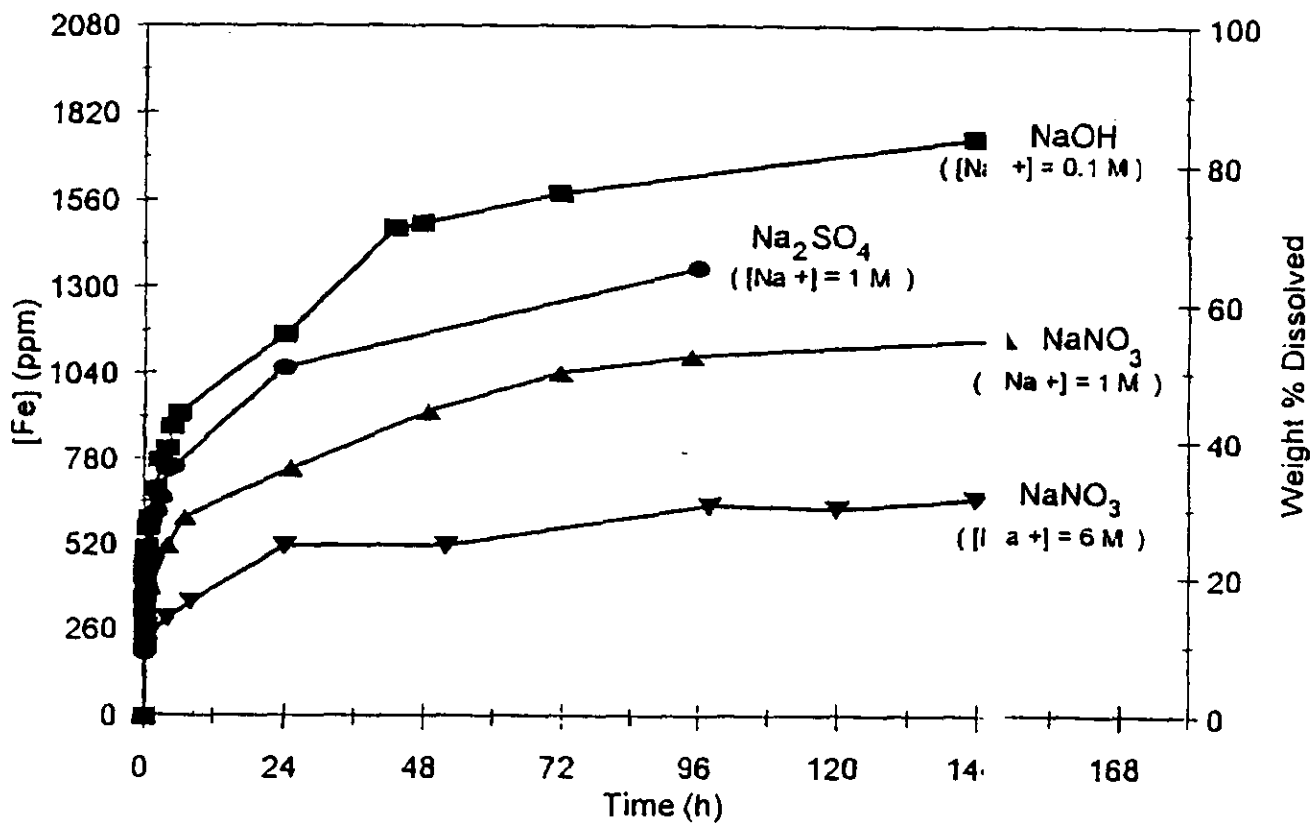
3.5 PLANNED WORK

The goal of the aging studies is to clarify the present condition of ferrocyanide sludge in Hanford Site SSTs. Understanding aging pathways will help interpret analytical results from supernatant, core, and vapor sampling. Knowing reaction rates and kinetic data under various temperature, concentration, and pH regimes should produce an approach for estimating current ferrocyanide concentration.

Preliminary dissolution, hydrolysis, and radiolysis experiments will be performed in FY 1993. A modeling effort to determine if microconvective mixing might have accelerated contact between ferrocyanide sludge and highly alkaline solutions added later to the SSTs is also being performed in FY 1993. The intent of these tasks is to (1) determine whether aging is possible; and (2) validate the chemical equations found in the literature under conditions simulating those which have existed in the ferrocyanide SSTs. Experiments completed in FY 1993 will be used to define the scope of experiments continued into FY 1994.

Experiments are investigating the effect of temperature, ionic strength, gamma radiation, and alkalinity on the dissolution, hydrolysis, and degradation of vendor-prepared sodium nickel ferrocyanide and the ferrocyanide flowsheet simulants. Studies in FY 1994 will attempt to define reaction rates and the chemical kinetics associated with dissolution and hydrolysis. A detailed test plan describing the work planned has been published as a PNL document (Lilga and Schiefelbein 1993).

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## 4.0 FERROCYANIDE SAFETY ISSUE RESOLUTION STRATEGY

To put the role of aging into perspective, the logic that is being used by the Ferrocyanide Safety Program for resolution of the ferrocyanide safety issue is discussed in this section. To ensure safe storage of the ferrocyanide waste until final disposal is completed, the waste must remain in a non-reactive form. Three alternative conditions can bound safe storage in any given ferrocyanide tank. They relate to (1) the presence of a dangerous amount of fuel inventory in the oxidizer-rich waste; (2) potentially dangerous concentrations of fuel and oxidizer, or the ability to control tank conditions to prevent a dangerous reaction from initiating. To resolve the safety issue, it must be demonstrated on a tank-by-tank basis (or on a group of tanks) that the tank contents are either:

- Intrinsically safe--The tank contains an insignificant (low) fuel inventory

- Passively safe--The tank contains a low fuel concentration

- In a state of controlled safety--The fuel concentration is sufficient for a reaction if the waste is dry and a high temperature is present, but temperature and moisture control are guaranteed (having an effective monitoring and corrective system in place). In addition, controlled safety requires that the controlled conditions can be maintained over the long term for all tank farm operations.

If the above criteria cannot be met, the tank's contents may be subject to mitigation or at least fall into a category of tanks for a candidate for early retrieval and remediation. A diagram of the in situ safe storage logic is presented in Figure 4-1.

The factors affecting the judgment of safety for the ferrocyanide- containing tanks (inventory, concentration, and/or control limits) are presented in Table 4-1. No single source of data is likely to provide sufficient proof of safety for any given tank other than those tanks that either received an insignificant inventory of fuel or were emptied of the suspect materials. Rather, a case must be established and documented showing where the preponderance of data and analyses clearly suggest that continued storage of the waste is safe under specified operating safety requirements.

Figure 4-1. Logic Determining In Situ Safe Storage of Ferrocyanide
Waste in Hanford Site Single-Shell Tanks.
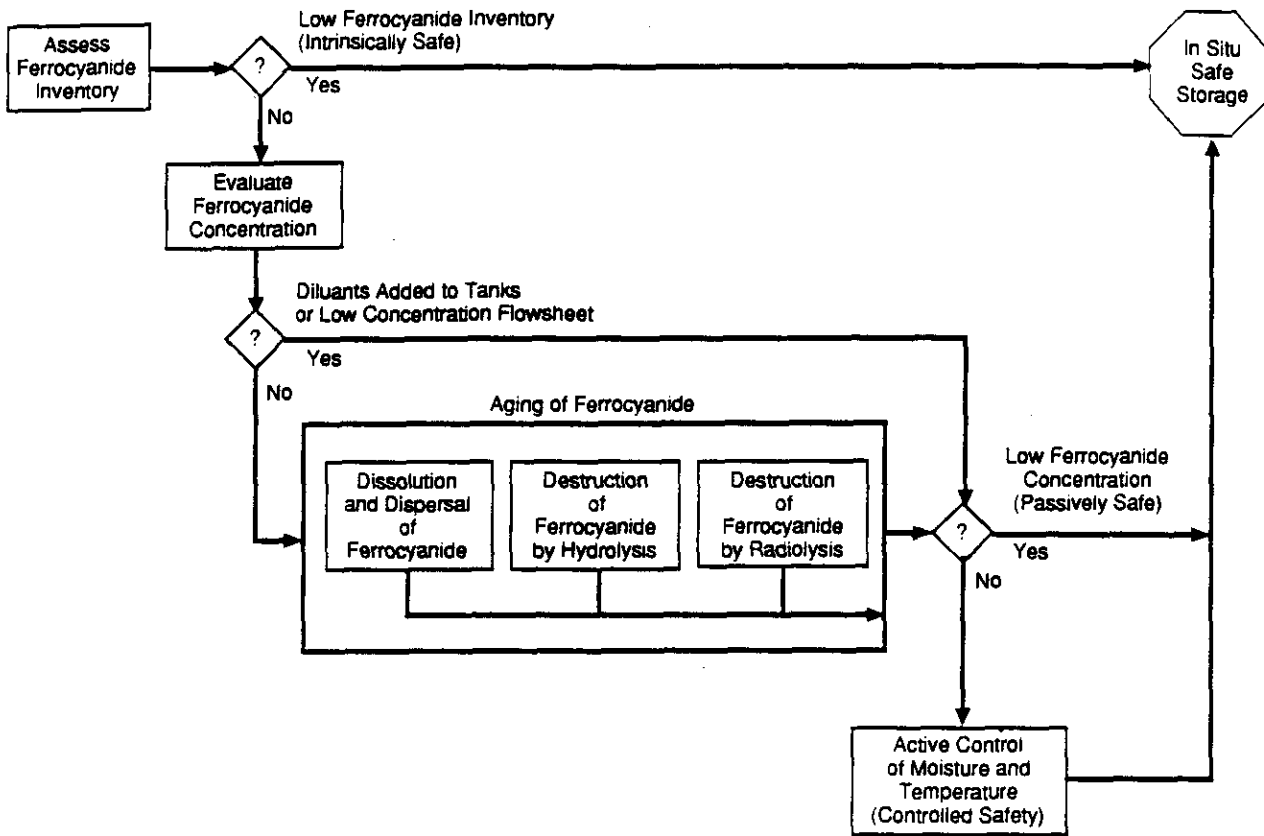
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Table 4-1. Information Sources Associated With Evaluation of Safety
Factors for Ferrocyanide Tanks.

SAFETY FACTOR	DATA SOURCE	INFORMATION NEED[1]
INVENTORY LIMIT	• HISTORICAL INFORMATION	• INVENTORY ESTIMATES FROM TRANSFER RECORDS • FLOWSHEET INVENTORY PROJECTIONS
	• WASTE CHARACTERIZATION DATA	• CHEMICAL AND PHYSICAL PROPERTIES FROM TANK SAMPLES
	• MODELING	• TRANSIENT AND MAXIMUM TEMPERATURE ESTIMATES OF FERROCYANIDE CONTAINING TANKS UNDER NORMAL AND "HOT SPOT" CONDITIONS
	• SIMULATED WASTE STUDIES	• THERMODYNAMIC ENERGY ESTIMATES • ACTUAL ENERGY DENSITY MEASUREMENTS OF FLOWSHEET SIMULANTS • DEGRADATION OR DECOMPOSITION (AGING STUDIES)
CONCENTRATION LIMITS	• HISTORICAL INFORMATION	• FLOWSHEET ANALYSIS • CONCENTRATION FACTORS
	• WASTE CHARACTERIZATION DATA	• MULTIPLE POINT WASTE MEASUREMENTS TO DEFINE WASTE CONCENTRATION PROFILES • LIQUID AND SOLID SAMPLE ANALYSES • MOISTURE MEASUREMENTS
	• MODELING	• THERMODYNAMIC ENERGY ESTIMATES • THERMAL MODELING OF TANK RESPONSES • ESTIMATES OF TANK FLUID MIXING (e.g., MICROCONVECTION)
	• SIMULATED WASTE STUDIES	• SIMULATED WASTE STUDIES - FUEL DISPERSION MECHANISM - DEGRADATION PATHWAYS - FUEL CONCENTRATION PATHWAYS - INITIATORS AND CATALYSTS
CONTROL LIMITS	• HISTORICAL INFORMATION	• ANALYSIS OF TANK RECORDS
	• WASTE CHARACTERIZATION DATA	• WASTE SURFACE SAMPLE ANALYSIS (SURFACE MOISTURE AND TEMPERATURE) • CONCENTRATIONS OF KEY CONSTITUENTS
	• MONITORING DATA	• ENHANCED TANK MOISTURE MONITORING DATA • ENHANCED TEMPERATURE MONITORING DATA
	• ENERGETICS AND REACTION DYNAMICS	• THERMODYNAMIC ENERGY ESTIMATES • THERMAL AND STRUCTURAL MODELING OF THE TANKS

[1]The data needs defined are not mutually exclusive. For example, characterization-based data may serve to prove that a tank contains a low inventory of ferrocyanide or that the concentration of ferrocyanide is low.

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5.0 CONCLUSION

Ferrocyanide-containing SSTs at the Hanford Site have been exposed to highly alkaline solutions. Experiments with ferrocyanide sludge simulants and vendor-prepared sodium nickel ferrocyanide have demonstrated that ferrocyanide will dissolve in caustic solution. Soluble ferrocyanide could have diffused or been convected into the bulk of the waste and subsequently diluted during waste transfer operations. Chemical and radiolytic aging may have converted the ferrocyanide to lower energy reaction products. Transferring soluble ferrocyanide to highly alkaline DSTs, as part of the Hanford Site stabilization program, would enhance chemical decomposition by bypassing a need for a diffusion or microconvection mechanism within the current ferrocyanide tanks.

Data on vendor-prepared sodium nickel ferrocyanide and results from core sampling of tanks 241-C-109 and 241-C-112 support the supposition that aging of ferrocyanide has occurred in the tanks during their 35-year storage period. However, while all conclusions supporting aging are encouraging, they are also tentative. Key portions of the ferrocyanide research program, when completed, will clarify the aging mechanisms.

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